



## Really, how significant is hydrogen-bonding in supramolecular association in molecular crystals?

Edward R.T. Tiekink

Research Centre for Crystalline Materials  
School of Science and Technology

Acad. Ionel Haiduc at the age of 80 - Cluj 2017

## Molecular packing

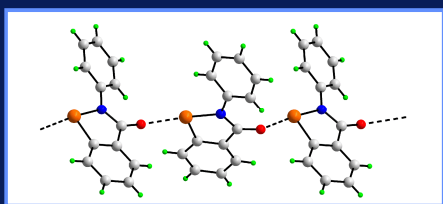
Well known...

Hydrogen bonding  
Halogen bonding

"Emerging"

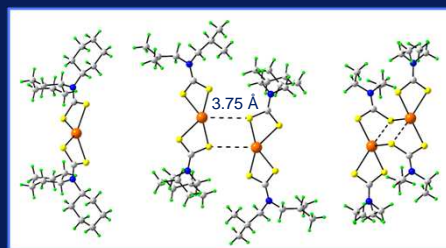
Secondary bonding  
M...M interactions  
M...H interactions  
Interactions involving chelate rings

## Tetrel, Pnictogen and Chalcogen Secondary Bonding



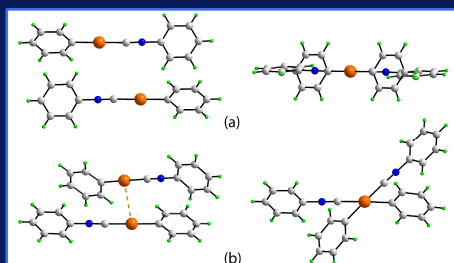
Se...O in Ebselen®  
polar gap,  $\sigma$ -hole; ~8 kcal/mol

## Steric effects and secondary bonding



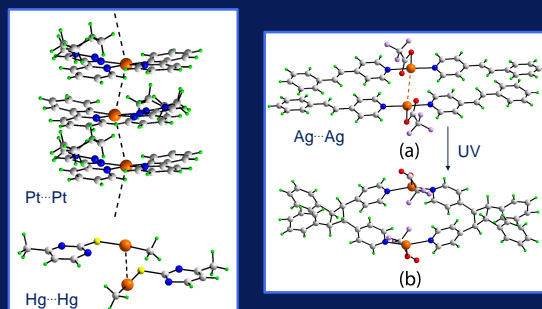
"Hg(S<sub>2</sub>CNR<sub>2</sub>)<sub>2</sub>"  
Sum of the van der Waals radii for Hg and S = 3.35 Å

## Aurophilic (Au-Au) interactions

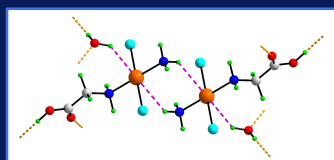


Polymorphs of PhAuC≡NPh  
(a) to (b) touch of a needle / mechanical grinding

## Heterometallophilic (M-M') interactions

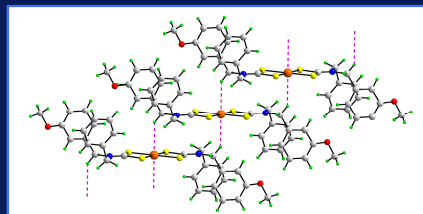


### Metal...hydrogen interactions as supramolecular synthons



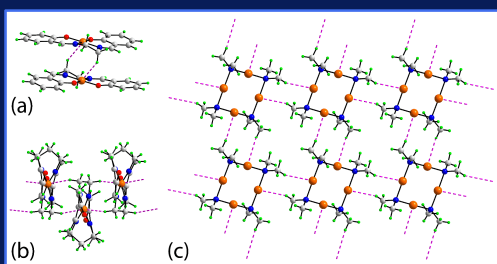
Pt...H-N and Pt...H-O hydrogen bonding in trans-[PtCl<sub>2</sub>(NH<sub>3</sub>)(N-glycine)]

### Metal...hydrogen interactions as supramolecular synthons



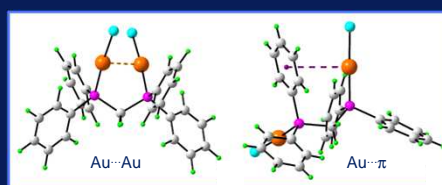
Ni...H interactions in Ni(S<sub>2</sub>CNR')<sub>2</sub>

### Metal...hydrogen interactions as supramolecular synthons



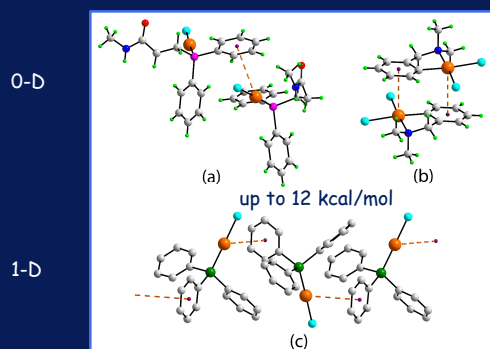
Architectures sustained by {...HCNM}<sub>2</sub> synthons

### Au...π(arene) interactions

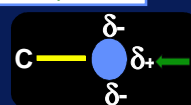
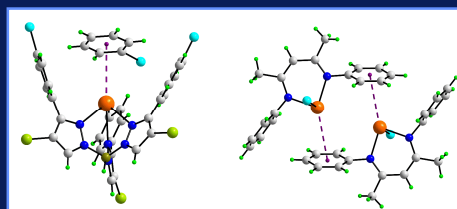


Polymorphs of (Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)(AuCl)<sub>2</sub>

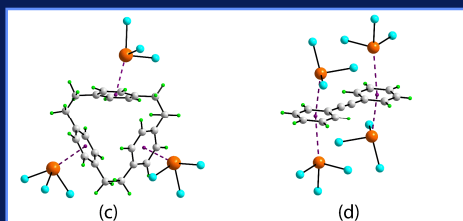
### Intermolecular Au...π(arene) interactions



### Intermolecular M(lp)...π(arene) interactions

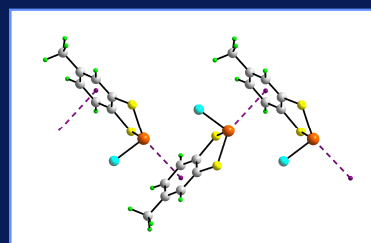


### Intermolecular $M(lp) \cdots \pi(\text{arene})$ interactions

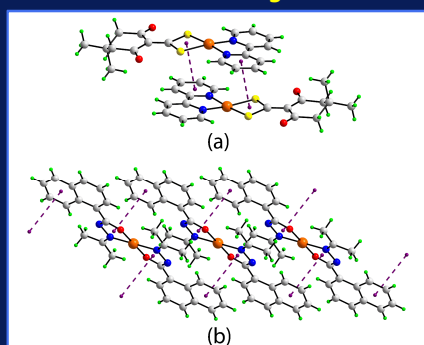


up to 10 kcal/mol

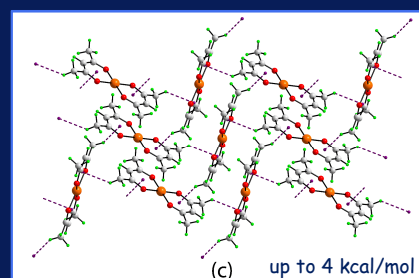
### Intermolecular $M(lp) \cdots \pi(\text{arene})$ interactions



### Intermolecular interactions involving chelate rings

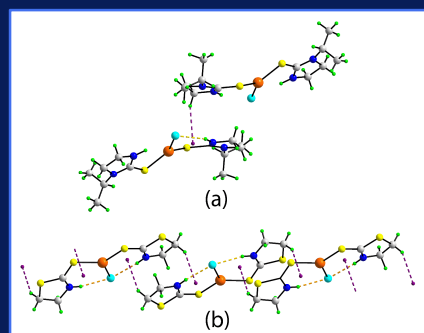


### Intermolecular interactions involving chelate rings



up to 4 kcal/mol

### Intermolecular interactions involving quasi-chelate rings



### Conclusions

More than hydrogen bonding

Energies of "emerging" interactions similar

<http://dx.doi.org/10.1016/j.ccr.2017.01.009>

## Sunway University



EDUCATION GROUP  
Based and governed by the  
Malaysian Chinese  
Foundation  
Incorporated in Malaysia

Fortuna Eruditis Favet ("Fortune favours the prepared mind")

## Announcement



**7<sup>th</sup> Asian Conference on Coordination Chemistry (ACCC7)**  
**22-26 July 2019 / Kuala Lumpur, Malaysia**  
**(Organised by Institut Kimia Malaysia)**

You are welcome to visit the conference's website at [www.accc7.org.my](http://www.accc7.org.my) for updates on ACCC7 or you can email us at [accc7@ikm.org.my](mailto:accc7@ikm.org.my) for further details.